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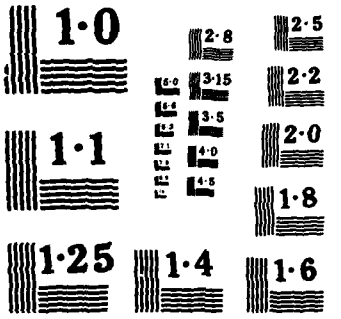

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In our search for metals with strong catalytic activity in promoting the oxidation of semiconductor surfaces, we have recently examined low electronegativity metals such as Sm, Cs and Na. Our preliminary studies show that Sm overlayers appear to yield the maximum oxidation promotion observed to date on the Si(111) surface. We have therefore focused on the Sm chemisorption process, that follows a peculiar two-step sequence on Si(111) and GaAs (110) surfaces. At submonolayer metal coverage Sm atoms are in a mostly divalent

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state. At higher metal coverages trivalent Sm specis dominate. At least in the case of Si the oxidation promotion effect appears related to the appearance of the trivalent state. This complex chemisorption process is still far from being completely understood. In this paper we present a simple experimental technique to study the electronic structure of metals in cluster or thin film form on ideally inert substrates. We apply this technique to Sm and we make systematic comparisons of the results for Sm chemisorption onto semiconductors surfaces and Sm adsorption onto inert substrates (solid Xe). In this first preliminary paper we give a very brief summary of the experimental technique and present selected results on cluster-size induced valence transition and on size-dependent metal screening during Sm adsorption on Xe.

Keywords: [illegible] Clusters; Metal Semiconductor [illegible]

SUMMARY ABSTRACT

EXPERIMENTAL DETERMINATION OF THE ELECTRONIC STRUCTURE OF SMALL METAL PARTICLES

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The electronic structure of small metal particles and the modification of this electronic structure that derive from interaction with a substrate are of prime concern to all of us working in the area of catalysis and chemisorption. In recent years we have conducted a number of chemisorption studies involving metal-semiconductor interactions [1] where one attempts to correlate the changes in adatom and substrate electronic structure (core and valence levels) to the rather complex chemistry of the metal-semiconductor interface. Since large modifications of the metal states are expected also as a result of the increase in cluster size and/or overlayer thickness when a fully inert substrate is employed, the interface scientist is obliged to look for systematic correlation between changes in substrate and adatom electronic features in order to extract the information pertaining to interface chemistry. It is clearly very desirable to compare the results of any chemisorption study on "reactive" substrates with those of similar studies conducted on ideally inert substrates. However, "inert" substrates are hard to come by, and the available experimental information is very scarce. The importance of such studies is emphasized by the discomforting observation that virtually all studies of interface chemistry tend to produce "chemical" shifts of electronic levels and no evidence of size-induced effects in the overlayer states.

In the past the search for an ideally inert substrate has stimulated the use of materials as diverse as amorphous carbon, graphite, silica, layer compunds, etc.[2] Optical and transport studies have been recently supplemented by photoemission spectrosopy studies, that probe directly core and valence states of substrate and overlayer.[3-6] One promising pioneering study has shown the feasibility of synthesizing <u>in situ</u> metal clusters on solid rare

gases[7] and examine the electronic structure through conventional photoemission. Here we summarize the result of a first synchrotron radiation study of Sm clusters grown in <u>situ</u> on solid Xe crystals. Samarium was chosen because an extensive literature exist on the formation of clusters on amorphous carbon [6], on the electronic structure of Sm surfaces [8], and on the chemistry of Sm-semiconductor interfaces.[9-10] Spectroscopically, the Sm 4f emission is a sensitive probe of the local environment, and a valence transition is expected on going from isolated divalent Sm^{+2} atoms to the trivalent bulk.[6] The Sm^{+2} and Sm^{+3} configurations are easily distinguishable in photoemission since they give rise to final states multiplets widely spaced in energy.

A bellow-mounted closed-cycle refrigerator was used as sample manipulator. Films of Al or Sm were evaporated in situ on the polished Cu cold finger prior to cooling. The films (100-500Å thick) were kept at 15K during Xe condensation. Xe pressure in the 10^{-4}-10^{-7} torr range and total exposure in the 10-10^5 L range were explored. We monitored the attenuation of the characteristic substrate emission (Al 2p or Sm 4f levels) as a function of Xe exposure to calculate the thickness of the condensed Xe layer. Surprisingly we observed an exponential attenuation of the substrate emission with constant attenuation length throughout the 0-50L exposure range. Extrapolation to higher Xe coverages and escape depth values from the literature suggest that we were able to synthesize Xe layers in the 5-6000Å thickness range, that such films were stable in ultra-high vacuum on a time scale of several hours, and that the film thickness was uniquely determined by the overall Xe exposure in Langmuirs for a given substrate. Dramatic charging effects of the insulating Xe films were observed at thicknesses above 100Å, and for the cluster studies we used Xe films in the 40-70Å thickness range. Representative photoelectron energy

distribution curves (EDC's) for the 5p 5s and 4d emission from a 70Å Xe film condensed on Sm are shown in fig.1. The spectra have been recorded with a commercial double-pass cylindrical mirror analyzer and a thoroidal grating monochromator at the Synchrotron Radiation Center of the University of Wisconsin-Madison. The energy scale is referred to the substrate Fermi level. Similar results are obtained from Xe films condensed on Al. The only difference is a rigid shift of 1.8 eV to lower binding energies of all Xe spectral features. The shift reflects the variation in substrate work function and the alignment of the insulating Xe states to the vacuum level. We have also analyzed the evolution of the Xe core emission as a function of layer thickness to study relaxation effects induced by metal proximity. On Al we measure relaxation shifts of 0.5eV between the first and the second Xe layer, and of about 0.2eV between the second and the third layer. The shift appear smaller in the Xe-on-Sm case, suggesting a different spatial extension of the screening orbitals.

When a metal is evaporated onto the Xe surface, the small substrate-overlayer interaction results in agglomeration of the deposited film and cluster formation. This is readily visible in the EDC's, since even at the highest coverages explored the Xe emission is always visible. The attenuation of the Xe emission as a function of coverage can be used to estimate the average size of the metal clusters, purview that one makes some simplifying assumption on the cluster morphology. We assumed hemispherical cluster size[11] and through escape-depth dependent core level studies of substrate and metal emission we were able to obtain rough estimates of the average cluster radius. The information on the cluster electronic structure is provided by valence band EDC's after subtraction of the Xe contribution. The result is

shown in fig.2 where we compare the cluster valence emission at increasing metal coverage with the bulk Sm emission (topmost EDC) from a 450Å-thick film deposited on oxidized Ta. The vertical bars indicate the Sm^{+2} final state mutiplet near the Fermi level and the deeper Sm^{+3} mutiplet.[11] The Xenon layer was condensed on a Sm film in an original "sandwich" geometry that minimizes work function-related shifts and simplifies the subtraction of the Xe features. The results of fig. 2 clearly show the expected valence transition from a dominant Sm^{+2} configuration at small cluster size, to a metallic Sm^{+2}/Sm^{+3} ratio (topmost EDC) at larger cluster size. From the modeling of the Xe core emission described previously we estimate an average cluster diameter of about 30 ± 8 Å at Sm coverages of 5×10^{14} atoms/cm^2 in fig.2 .[11]

In conclusion, we have presented a simple, straightforward technique to study cluster evolution. From escape-depth-dependent synchrotron radiation photoemission we can estimate cluster distribution and average cluster size. As a by-product of the Xe-metal interaction we obtain information on metal screening and work function[12]. The simplicity of the technique offer promise of wide-range systematic studies in the near future.

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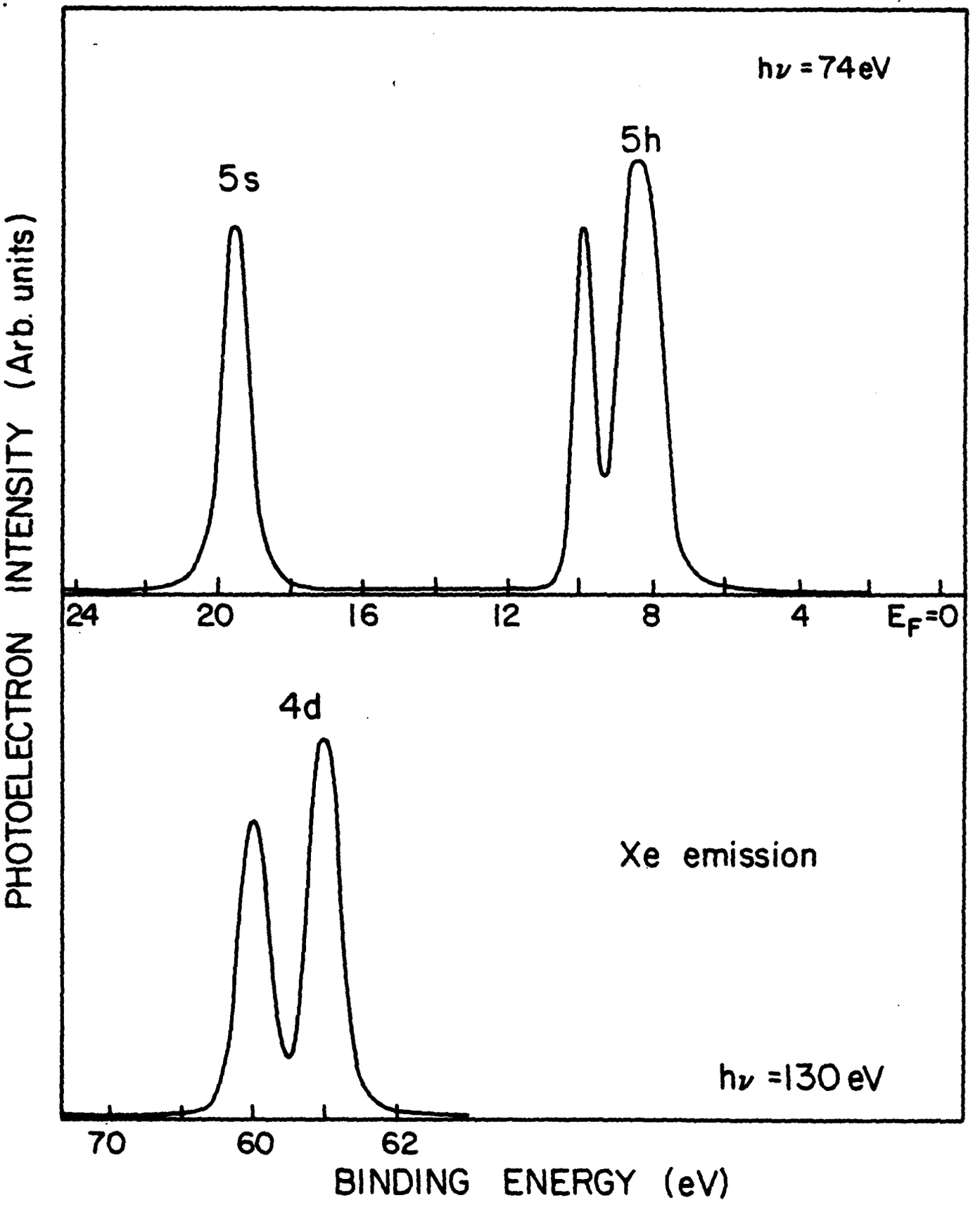
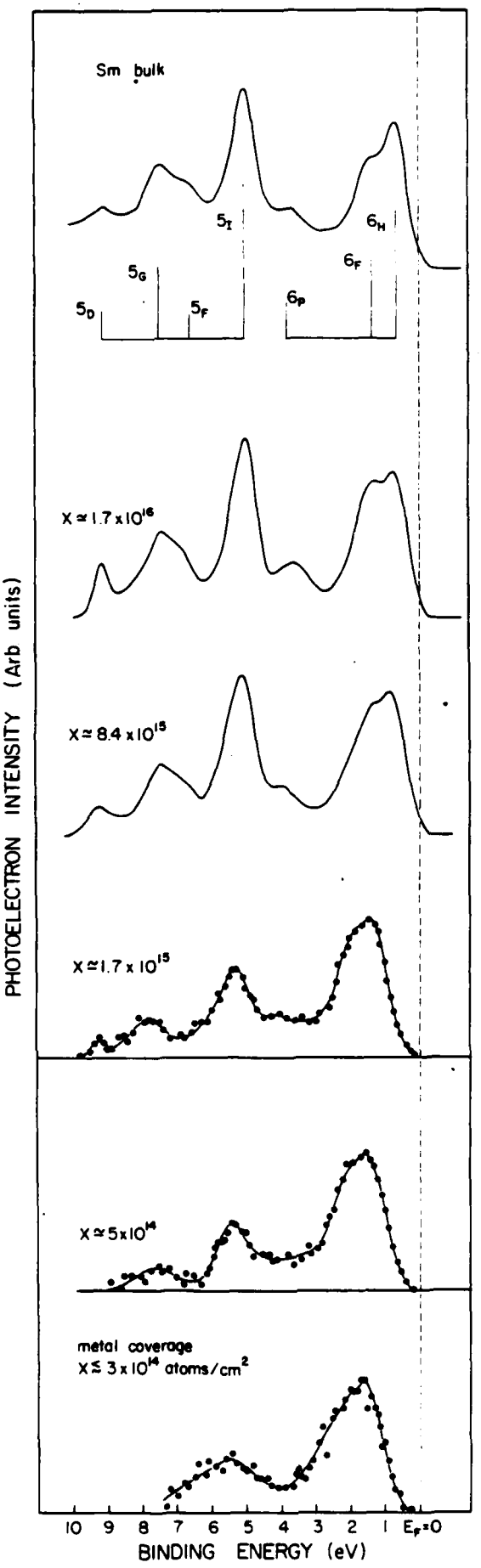
FIGURE CAPTIONS

Fig.1 Emission from the Xe 5p, 5s and 4d levels from a 50Å amorphous film condensed on a clean Sm substrate at 15K.

Fig.2 Valence band emission from Sm clusters deposited in situ on a solid Xe substrate. The spectra are shown after subtraction of the Xe 5p contribution. The topmost spectrum was obtained from a 450Å thick Sm film deposited at room temperature on oxidized Ta. The vertical bars indicate the 4f final state multiplets for the Sm^{+2} and Sm^{+3} configurations. A valence transition from a dominant divalent Sm configuration to a dominant trivalent configuration is seen with incresing cluster size.


hν = 74eV
5h
5s
PHOTOELECTRON INTENSITY (Arb. units)
24
20
16
12
8
4
E_F=0
4d
Xe emission
hν =130 eV
70
60
62
BINDING ENERGY (eV)


Sm bulk
5_I
6_H
5_G
6_F
5_D
5_F
6_P
X ≃ 1.7 x 10^16
X ≃ 8.4 x 10^15
X ≃ 1.7 x 10^15
X ≃ 5 x 10^14
metal coverage
X ≤ 3 x 10^14 atoms/cm^2
PHOTOELECTRON INTENSITY (Arb units)
10 9 8 7 6 5 4 3 2 1 E_F=0
BINDING ENERGY (eV)

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